Triptycene Diols: A Strategy for Synthesizing Planar π Systems through Catalytic Conversion of a Poly(p-phenylene ethynylene) into a Poly(p-phenylene vinylene)
Conjugated Polymer Reactivity

Triptycene Diols: A Strategy for Planar π-Systems Demonstrated by the Catalytic Conversion of a PPE into a PPV**

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The performance of conjugated electronic polymers is highly dependent on conformation and the limits it places on electronic delocalization. Coplanarity of adjacent segments is generally desired to create the highest π-orbital overlap, resulting in less energetic disorder along the backbone. Simply stated, enforced planarity of the π-system leads to greater exciton and charge transport (along the π-way).[1] Greater chain coplanarity can be achieved by simply polymerizing fused polycyclic planar, π-extender monomers. Alternatively, post-polymerization annulation and rigidification, often taking advantage of reactive side chains,[2] has proven an effective strategy—particularly for phenylene-based ladder polymers.[3]

Recently, our group reported an efficient synthesis of triptycene diols (TDs, 1a) using a Rh-catalyzed [2 + 2 + 2] cycloaddition.[3] The rigid three-dimensional structure of triptycene derived scaffolds have proven to be a versatile motif for creating new and enhanced material properties.[4] To expand the diversity of iptycene scaffolds for such applications, we envisioned a suitably functionalized TD (1b) might be amenable to further functionalization through Pd cross-coupling methods (Scheme 1b–2). The resultant extended π-system (2) has close proximity to the hydroxyl group, affording the opportunity for cyclization reactions to create higher-order planarized triptycene π-systems (Scheme 1, 2→3).

To investigate this strategy for cyclization and planarization we have targeted alkyl π-systems as a result of the significant literature regarding alcohol-alkyne cyclization reactions (Scheme 4.1, 4→5→6).[5] Further, in the context of polymer chemistry, we envisioned such a transformation might also provide a post-polymerization means of converting the alkylene units of readily available poly(phenylene ethynylene)s (PPEs)[6] to give a new class of poly(phenylene vinylene)s (PPVs)[7] with anulated alkene units (vide infra, Scheme 5). This transformation represents a particularly rare form of post-polymerization reactivity for conjugated polymers as the polymer main chain would be chemically altered (in contrast to modification or elaboration of side chains).

Within the context of PPE main chain alteration, the literature is sparse and the best examples are full[8] and partial[9] hydrogenation of the triple bonds to give respective unconjugated poly(p-xylylene)s and cis-poly(p-phenylene vinylene)s (PPVs). The transformation outlined in Scheme 1 would result in a trans-PPV. Further, it would provide for a rare substitution of the vinylene segment[10] of a PPV with an electron donating oxygen group, while simultaneously creating greater planarity in the backbone. Herein we detail the synthesis and transformation of 1b to give molecules and polymers with planarized extended π-systems.

The synthesis of TDs—bearing the 1,4-halogen substitution pattern (1b)—used the previous [2 + 2 + 2] cycloaddition strategy.[3] However, the presence of bromine substituents did not permit direct transfer of previous synthetic conditions, and a modified synthesis is presented herein (Scheme 2). Starting from commercially available 7, a Sandmeyer reaction[11] afforded dibromoanthroquinone 8 in excellent yield. Double addition of lithium TIPS acetylide to 8 in toluene provided the syn-addition product (9) with modest selectivity (2:3:1 syn:anti). The analogous lithium TMS acetylide gave a mixture of 1:1 syn:anti addition products. Isomers are separable by chromatography). Finally, fluoride deprotection gave the cyclization substrate 10.

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Scheme 1. Rationale for the conversion of triptycene diols in cyclization reactions to give planar extended π-systems.

Scheme 2. Synthesis of 1,4-dibromo substituted triptycene diols.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
The previously effective Wilkinson’s catalyst [Rh(PPh₃)Cl] failed to give [2 + 2 + 2] cycloaddition products for 10. However, the ruthenium catalyst [CpRu(PPh₃)₂Cl] readily produced [2 + 2 + 2] cycloadditions with terminal alkynes to yield racemic products (11–13). Finally, the formal cycloaddition with acetylene was obtained (1b) by reaction of norbornadiene in the presence of [Rh(cod)Cl]₂, via a [2 + 2 + 2] cycloaddition followed by a retro-Diels–Alder reaction and expulsion of cyclopentadiene (12).

Compound 14 was investigated as a direct precursor to a polymerizable monomer (for PPEs) and was synthesized in a straightforward manner from 1b via Sonogashira coupling with a TMS protected acetylene (Scheme 3). However, upon deprotection with either fluoride or basic methanol, spontaneous metal-free cyclization occurred on one side of the molecule to give 15. NMR analysis indicated the product to be the 5-exo-dig cyclization (based on vinyl coupling constants), and X-ray crystallography revealed how closure of the five-membered ring creates a geometry that pulls the other alkylene and hydroxyl apart to prevent a second cyclization. We reasoned that cyclization of the alcohol oxygen onto the terminal carbon of the alkylene (6-endo-dig) would lead to a less strained 6-membered ring with less structural distortion and might allow for double cyclization (Scheme 1). To this end, the phenyl acetylene analogue 16 was found to be indefinitely stable to spontaneous cyclization, which allowed for exploration of selective 6-endo-dig cyclization through electrophilic activation of the alkylene (Scheme 3).[13]

Treatment with electrophilic iodine sources provided the doubly cyclized product with concomitant installment of iodides on the alkene.[14] Further, electrophilic gold(III) proved moderately effective in promoting the 6-endo-dig isomerization of 16 into the mono- and doubly cyclized compounds 18 and 19. These observations, along with the X-ray crystal structure of 19 shown in Scheme 3, confirm our hypothesis that the 6-endo-dig pathway enabled double cyclization to take place. Further, the dihedral angles between the newly formed rings and terminal benzenes were near planarity (1.1 ± 0.8° and 3.4 ± 0.4°). This planarity derives from the less sterically demanding oxygen lone pairs—in contrast to an analogous biphenyl system—and bonds well for increased monomer coplanarity in polymer 24 (vide infra).

Compound 19, with its rigidified structure, displayed poor solubility making analysis and further method development difficult. To address this issue, compound 14—bearing a solubilizing alkyl side chain—was employed to give bis(phenyl acetylene) 20 (Scheme 4). Subsequent optimized 6-endo-dig isomerization of the alkylene to the oxygen substituted alkene 20–21 using a more active gold(I) catalyst system[15] provided 21 in high isolated yield (the reaction displayed spot to spot conversion by TLC). The high conversion and lack of side-products gave us confidence that we could extend this method to the post polymerization alteration of PPEs into PPVs. Additionally, the resistance to spontaneous cyclization provided by 20 (and 16) ensures the synthesis and characterization of well-defined PPEs (free of cyclized “defects”), which could then be catalytically isomerized to the PPVs.

We selected 12 and 22 as monomers for the Sonogashira polymerization to form PPE 23 (Scheme 5). Compound 22 was an attractive monomer as it lacked side chain substitution on the benzene ring that would adversely affect chain planarity through steric interactions. However, the lack of side chains also presents a challenge for solubility as side chains are typically used to promote polymer solubility. We hoped to offset this issue using the characteristics of comonomer 12, with disorder in the solubilizing n-octyl side chain arising from its racemic nature and an expected region-random orientation in the polymer chain. Additionally, the rigid three-dimensional structure of iptycenes (tritycene in this case) has been observed to impart greater solubility through suppression of interpolymer π-π associations.[16] The polymerization (Scheme 5) successfully produced polymer 23 at reasonably high molecular weight (Mₐ = 12,500, PDI = 1.44, DP = 24). However, the isolated yield of soluble 23 was low (32%) due to large quantities of insoluble—presumably high molecular weight—polymer.[17] In any case, 23 was subjected to a two-stage addition (see Supporting Information for details) of gold(I) catalyst to produce cyclized polymer 24 (Mₙ = 14,700, PDI = 1.16 DP = 28). The increase in molecular weight of 24 relative to 23 was likely due to increased rigidity along the polymer chain. This rigidity increases the persistence length of the polymer, making it appear larger under size dependent measurements (i.e. GPC).[18, 19]

The effects of the cyclization reaction on the π-systems of 21 and 24 were most distinctly visualized in their UV-vis and fluorescence signatures relative to their respective starting materials (Figure 1). Model substrates 20 and 21, both showed very small Stokes shifts, however the absorbance and fluorescence maximum of 21 are red-shifted by almost 100 nm after cyclization (Figure 1a) and (Table 1). This closing of the band gap is ascribed to both the increased planarity of 21 and the presence of electron rich oxygen donor atoms on the alkylene that raise the HOMO level. The distinctly sharper emission features of 21 and resolved vibrational transitions also evidenced the increased rigidity (enforced planarity).[19] As expected there is also an associated increase in fluorescence quantum yield for 21 compared to 20, as a result of the removal of vibrational relaxation through planarization and rigidification.
Both polymers remain visibly fluorescent in thin film (Table 1), and found in the Supporting Information.

The compounds discussed above differ from previous oxygen substituted PPV systems in that the substitution occurs on the vinyl unit instead of the phenyl. To understand these substitution effects, we performed DFT calculations for the LUMO and HOMO of 19 (Figure 1d and e). These data show the closing of the band gap for each compound may stem more from the planarization than from the oxygen substitution. In both the HOMO and LUMO there is only a small electron density on the oxygen. The band gap of 21 was similar to other ring substituted triphenylenevinylene model systems. However, the band gap of 24 was larger than for MEH-PPV, which may result from possessing half the oxygen substitution per repeat unit relative to MEH-PPV.

To summarize, we have developed a highly efficient method to introduce planarity and rigidity along a conjugated polymer backbone using a catalytic main chain alteration to convert the alkynes of the PPE (23) into annulated alkenes in the PPV (24)—transitioning between two classes of conjugated polymer. The post-polymerization cyclization provides for a rarely seen oxygen substitution of the vinyl units of a PPV and endows the products with greater planarity and rigidity, resulting in red shifts in absorbance and fluorescence and defined vibrational features. We hope to extend this cyclization strategy to establish higher order planarity for other conjugated polymer classes.

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In contrast to 21, polymer 24 did not have an associated increase in fluorescence quantum yield relative to precursor polymer 23. This may be related to the lower fluorescence lifetime ($\tau_2$) of 24, which is almost double that of 23 (Table 1), and the lower band gap. As a result, 23 showed a higher quenching response (KSV = 511) to 2,4-dinitrotoluene (DNT) than did 24 (KSV = 92). Further discussion of the mode of quenching with respect to fluorescence lifetime can be found in the Supporting Information.

The thin film spectra for both polymers are shown in Figure 1c. Both polymers remain visibly fluorescent in thin film (Table 1), and 24 maintains a significant red shift relative to 23. It would appear that the triptycene group—the smallest member of the iptycene family—was not sufficient to prevent unfavorable π-π interactions between polymer chains as both polymers display significant broadening of their absorbance and fluorescence spectra. However, the rigidified polymer 24 appears to retain vibrational structure in its thin film fluorescence spectrum (Figure 1c).

Table 1. Summary of photophysical data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs $\lambda_{max}$ [nm]</th>
<th>Em $\lambda_{max}$ [nm]</th>
<th>log $E_0$</th>
<th>$\Phi_F$</th>
<th>$\tau_F$</th>
<th>$E_{optical}$ [eV]</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>322</td>
<td>349</td>
<td>4.74</td>
<td>0.65</td>
<td>1.11</td>
<td>3.5</td>
</tr>
<tr>
<td>21</td>
<td>395</td>
<td>427</td>
<td>4.63</td>
<td>0.89</td>
<td>1.77</td>
<td>2.8</td>
</tr>
<tr>
<td>23</td>
<td>372</td>
<td>408</td>
<td>4.62</td>
<td>0.74</td>
<td>0.53</td>
<td>2.8</td>
</tr>
<tr>
<td>24, film</td>
<td>460</td>
<td>507</td>
<td>5.23</td>
<td>0.46</td>
<td>1.28</td>
<td>2.4</td>
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<tr>
<td>23, film</td>
<td>384</td>
<td>485</td>
<td>0.15</td>
<td>1.20</td>
<td>0.53</td>
<td>2.8</td>
</tr>
<tr>
<td>24, film</td>
<td>435</td>
<td>523</td>
<td>0.03</td>
<td>1.10</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

[a] Measured in CHCl$_3$. [b] Determined from abs $\lambda_{max}$. [c] Band gap, estimated by onset of absorption spectrum. [d] Biexponential lifetime 62.9%, second exponential 3.5 ns, 17.1%. [e] Biexponential lifetime 91.7%, second exponential 3.0 ns, 8.3%.


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[19] Additionally, consistent with triphenylene vinylene systems, the (0,0) transition of 21 was not the most intense band in the absorption spectrum (Figure 1a), but was the most intense in the emission spectrum. This indicates the terminal phenyl rings for 21 may not be coplanar in the ground state but are so in the excited state.


[21] A brief description of the electrochemistry of 21 and 24 can be found in the Supporting Information.
A strategy for introducing greater chain coplanarity is demonstrated in the synthesis of a new class of poly(p-phenylene vinylene) (PPV) bearing annulated alkene units from a parent poly(p-phenylene ethynylene) (PPE). The reaction involves a gold-mediated cycloisomerization of the PPE alkynes with hydroxyl group reacting partners held in proximity to the main chain. The result is a stark increase in chain rigidity and planarity, evidenced by pronounced photophysical changes.